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ОКИСЛИТЕЛЬНАЯ КОНВЕРСИЯ МЕТАНА НА КАТАЛИЗАТОРАХ ReO_X/Al_2O_3

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Образцы ReO_x/оксид алюминия исследованы в качестве катализаторов окислительной конверсии метана. Показано, что реакция метана с окисленным (1 ч), а затем вакуумированным при этой температуре (973 К, 1 ч) образцом приводит к образованию сначала главным образом C_2H_6, C_2H_4 и CO_2, а затем только CO и C_6H_6. Образование этана и этилена на начальной стадии реакции метана с образцами ReO_x /оксид алюминия является результатом реакции окислительной конденсации метана с образованием этана с последующим дегидрированием его в этилен. Реакция протекает с участием центров типа анион-радикала кислорода $O^{-\bullet}$ (V-типа дефект) структуры ReO_x/оксид алюминия ($CH_4+[O^{-\bullet}]= CH_3^{\bullet} +OH^-$; $2CH_3^{\bullet} = C_2H_6$). CO_2 образуется окислением метана с поверхностными кислородными формами (O_2^{2-} или/и $O_2^{-\bullet}$) оксидной структуры. Прямое окисление метана до метанола и дальнейшее расщепление последнего до CO и H_2 в нашем случае не исключаются: $CH_4 + ReO_x /Al_2O_3 = CO + 2H_2 + ReO_{x-1}/Al_2O_3$. Показано, что катализаторы, предварительно оокисленные при 973 К в течение 1 ч в кислороде и затем вакуумированные при этой же температуре в течение 1 ч, характеризуются спектрами ЭПР, принадлежащими парамагнитному иону Re^{6+} с $5d^1$ неспаренным электроном и сильной связью Re=O. Спектры ЭПР этого иона характеризуются разрешенной сверхтонкой структурой ($A_{\parallel}$ = 48,3 мТл) за счет взаимодействия неспаренного электрона с магнитными ядрами $^{185,187}Re$, имеющими спин I = 5/2 и легко наблюдаются при комнатной температуре для всех исследованных образцов. Сигналы ЭПР этих центров исчезают после взаимодействия образцов, вакуумированных при высокой температуре (973 К), с метаном. Было показано, что высокотемпературный контакт этого образца с метаном приводит к образованию центров, которые катализируют реакцию окислительной дегидроциклизации метана. Степень окисления ионов рения в этих образцах меньше 6+, и эти ионы являются координационно-ненасыщенными. Для поддержания активности катализатора требуется его регенерация. Активация катализатора достигается путем кратковременной термообработки его в токе кислорода с последующей продувкой инертным газом (азот, аргон).

Ключевые слова: катализаторы ReO_x/Al_2O_3, метан, окислительная конверсия, ЭПР спектры

OXIDATIVE CONVERSION OF METHANE OVER ReO_X/ALUMINA CATALYSTS

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ReO_x/alumina samples have been studied as catalysts for the oxidative conversion of methane. It was shown that the reaction of methane with an oxidized and then evacuated at this temperature (973 K, 1 h) samples leads to the formation of primarily C_2H_6, C_2H_4 and CO_2, and then only CO and C_6H_6. The formation of ethane and ethylene in the initial stage of the reaction of methane with ReO_x / alumina samples is the result of the reaction of oxidative condensation of methane with the formation of ethane, followed by its dehydrogenation to ethylene. The reaction proceeds with the participation of $O^{-\bullet}$ ion-radical type (V-type defect) centers of the ReO_x / aluminum-oxide structure ($CH_4 + [O^{-\bullet}] = CH_3^{\bullet} + OH^-$, $2CH_3^{\bullet} = C_2H_6$). CO_2 is formed by the oxidation of methane with surface oxygen forms (O_2^{2-} and / and $O_2^{-\bullet}$) oxide structure. Direct oxidation of methane to methanol and further splitting of the latter to CO and H_2 in our case are not excluded: $CH_4 + ReO_x/Al_2O_3 = CO + 2H_2 + ReO_{x-1}/Al_2O_3$. It was shown that catalysts preliminarily oxidized at 973 K for 1 h in oxygen and then evacuated at the same temperature for 1 h are characterized by ESR spectra belonging to the paramagnetic Re^{6+} ion with $5d^1$ unpaired electron and strong Re=O bond. The ESR spectra of this ion are characterized by a hyperfine structure ($A_{\parallel}$ = 48.3 mT) due to the interaction of an unpaired electron with $^{185.187}$Re magnetic nuclei having the spin of I = 5/2 and are easily observed at room temperature for all samples. The ESR signals of these centers disappear after the interaction of samples evacuated at high temperature (973 K) with methane. It was shown that high-temperature contact of this sample with methane leads to the formation of centers that catalyze the oxidative dehydrocyclization of methane. The degree of oxidation of rhenium ions in these samples is less than 6+, and these ions are coordinatively unsaturated. To maintain the activity of the catalyst, its regeneration is required. Activation of the catalyst is achieved by short-term heat treatment in oxygen flow followed by purging with an inert gas (nitrogen, argon).

Key words: ReO_x/Alumina catalysts, methane, oxidative conversion, ESR spectra

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INTRODUCTION

Methane is the most inert by reactivity among the hydrocarbons. A huge number of papers are published on homogeneous and heterogeneous systems, activating methane, over the last 25-30 years [1-3]. In homogeneous metal-complex, organometallic and micro-heterogeneous systems methane is quite easily activated even at room temperature [4, 5]. On the solids, methane is converted to different products at high temperatures, generally above 673 K. Therefore, interest

in the problem of catalytic activation of methane continues unabated to the present day [6, 7]. The number of the scientific papers which describe the catalytic conversion of methane into oxygen-containing compounds such as methanol and formaldehyde [7, 8], products of oxidative coupling – ethane, ethene [9, 11] increase each year. A lot of systems are described, which catalyze methane to aromatic hydrocarbons [12-22]. Despite of significant advances in this area, synthesis, preparation of efficient catalysts for the above reactions until today remain the main problems of the catalytic chemistry, petrochemistry, chemical engineering.

In this paper the data of EPR spectroscopy in combination with chromato-massspectrometry studies of ReO_x/Alumina oxide system as catalyst for the oxidative conversion of methane into benzene are presented.

EXPERIMENTAL PART

The samples of ReO_x/Alumina were prepared by impregnation of the amino-acids (glycine, cysteine) rhenium compounds from the weak hydrochloric aqueous solution followed by high-temperature processing. The elemental and phase composition of obtained catalysts are characterized using the atomic absorption spectrometer iCE-3000, Thermo Scientific, USA, X-ray diffractometer XRD TD-3500, China, X-ray fluorescence microscope XGT 7000, Horiba, Japan.

The ESR-spectrometer JES-PE-3X, Jeol, Japan and UV/Vis spectrometer, Analytik Jena, Germany, are used for to identification the electronic state of rhenium in the catalysts. Chromato-mass-spectrometer GC-MS, Focus, Thermo Scientific is used to determine the composition of gas phase products of the oxidative conversion of methane over these catalysts.

RESULTS AND DISCUSSION

Results of the testing of the obtained samples as catalysts for the oxidative conversion of methane are summarized in the table.

Table

Gas-phase products of oxidative conversion of methane over ReO_x/Alumina samples

Таблица.* Газофазные продукты окислительной конверсии метана на образцах ReO_x/Al_2O_3

Catalyst	Conversion of methane, %	Selectivity					Duration of the reaction, min.
		CO	C_2H_4	C_2H_6	ΣC_3	C_6H_6	
I	0.9	39.2	7.6	14.7	1.1	38.4	15
	0.5	50.1	4.8	24.1	1.7	19.2	45
	0.4	46.9	5.2	31.8	1.6	15.5	70
II	0.8	34.2	19.7	13.8	0.6	31.7	15
	0.6	35.9	12.8	29.7	0.4	21.2	45
	0.6	39.2	8.2	23.1	1.3	28.2	70
	1.0**	42.8	9.6	7.4	trace	41.1	15
	0.7**	42.7	7.7	17.9	1.2	32.9	45

Note: * Conditions of experiment: before testing the samples were purged with a flow of O_2 at 973 K (1h) and then helium (1h); reaction mixture: pure CH_4 (100%); T=923 K; residence time – 2.5 sec. ** After recalcination (1h) and treatment (1h) in a flow of He at 973K

Примечание: * Условия эксперимента: перед испытанием образцы продували O_2 при 973 К (1 ч) и затем Не (1 ч); реакционная смесь: чистый CH_4 (100%), Т = 923 К, время контакта - 2,5 с. ** После реокисления в атмосфере кислорода и продувки гелием при 973К

As can be seen from the table, the main products of the reaction are C_2H_6, C_2H_4, CO_2, CO and C_6H_6 and both catalysts show almost the same activity before and after re-calcination in air or oxygen. The samples were treated as indicated below to determine the active state of catalysts:

treated at 973 K for 1 h in oxygen and then reduced in hydrogen stream at 773 K for 5 h;

treated at 973 K for 1 h in oxygen and then evacuated at 973 K for 1 h;

treated at 973 K for 1 h in oxygen and then reduced with methane at the same temperature for 10 min;

treated at 973 K for 1 h and then reduced with methane at the same temperature for 1h.

It was established that the samples don't show the activity in the case (a) and (b), show the sufficient activity in the case (c) and decreased (d) activity in comparison with the case (c).

What happens with the catalysts subjected to the indicated above treatments?

The EPR spectra of the catalysts previously calcined at 973 K for 1 h in oxygen and then evacuated at the same temperature for 1 h show two types of paramagnetic centers (Figure). The first center belongs to paramagnetic ion of rhenium Re^{6+}, having the strong Re = O bond ("yl" – type). The ESR spectrum of this ion characterized with resolved hyperfine structure ($A_\parallel$ = 48.3 mT) due to the interaction of the unpaired electron with the magnetic nuclei ^{185,187}Re, having spin I = 5/2). The ESR spectrum of this center is easily observed at room temperature for the all investigated samples.

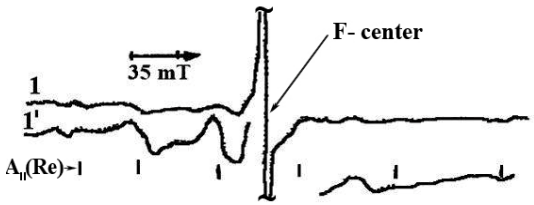

Fig. ESR spectra of ReO_x/Alumina sample calcinated in air at 973K for 2 h, then evacuated at the same temperature for 1 h and abruptly cooled to liquid nitrogen temperature
Рис. Спектры ЭПР образца ReO_x/Al_2O_3, прокаленного на воздухе при 973 К в течение 2 ч, затем вакуумированного при той же температуре в течение 1 ч и резко охлажденного до температуры жидкого азота

Diffuse reflectance electron spectra of samples are characterized by the intensive bands at 220-330 nm range.

Five points with a spot beam of 10 micron randomly chosen for scanning the surface show almost homogeneous distribution of rhenium on the surface of alumina. The γ-phase alumina is detected for both catalysts by XRD.

The content of rhenium in the catalysts determined by AAS was ~0,5wt.%. It was established that with a sharp cooling of the samples evacuated from 973 K to 77 K, in the EPR spectra measured at 77 K, along with the signal from the first center the second intense narrow signal with g = 2.001 and ΔH = 2.5 mT is observed. This center belongs to anionic vacancies with captured electron, ie. F-centers. The concentration of these centers is not less than 10^{19} spin/g. The formation of these centers in high-temperature evacuation of Re/Alumina oxidized samples due to dehydroxylation of the surface and appearance of structures ReO_x/Alumina with defects, having unpaired electron ($Re^{7+} + e \rightarrow Re^{6+}$ (center 1); $\cup + e \rightarrow$ F–center, where $\cup$ – anion vacancy (center 2).

At slow cooling of evacuated at 973 K ReO_x/Alumina samples to room temperature the ESR spectra for this center is not detected. This case can be explained by redistribution of the electrons in reduced by high temperature evacuation or interaction with methane samples as a function of cooling procedure of samples for EPR measurements.

Thus, we have two types of isolated from eachother magnetic centers in the samples oxidized at high temperature and then evacuated at the same temperature samples. The lack of a noticeable magnetic interaction between the centers 1 and 2 suggests that they are separated by a distance at which the magnetic interactions between these centers do not lead to a broadening of the signals from the centers 1 and 2. ESR signals from these centers disappear after interaction of the sample evacuated at high temperature (973 K) with methane at a temperature of evacuation. As a result of this procedure we have get the samples, which are active in the oxidative conversion reaction of methane. We can conclude that the active centers are interaction products of methane at high-temperature with ReO_x/Alumina oxide samples evacuated at the same temperature. The oxidaton degree of rhenium ions in these samples is less than 6+ and these ions are coordinatively-unsaturated. The rhenium catalyst activity depends essentially on the duration of the preliminary high temperature evacuation, during which the accumulation of coordinatively unsaturated, lower valence rhenium ions takes place. High temperature contact of this sample with methane leads to formation of the centers which catalyze the reaction of methane oxidative dehydrocyclization.

The studies show that at the first stage of the reaction of methane with evacuated at 973 K samples, mainly, C_2H_6, C_2H_4, and CO_2, and then almost only CO and C_6H_6 are observed. The formation of benzene is characterized by induction period with duration equal to formation and and disapppearace of CO_2 at the initial stage of reaction. The induction period depends essentially on the duration of the preliminary high vacuum treatment. With the increase in the duration of high-temperature vacuum treatment the duration of the induction period is reduced, and the interaction of rhenium catalyst with methane is accompanied with the formation of CO, which is the main product of the reaction of methane with rhenium catalyst:

$$CH_4 + ReO_x/Al_2O_3 \rightarrow CO + 2H_2 + ReO_{x-1}/Al_2O_3$$

The formation of ethane and ethylene at the initial stage of reaction of methane with ReO_x/Al-oxide samples is the result of oxidative coupling of methane to ethane and dehydrogenation of the latter to ethylene, respectively. Oxidative coupling of methane to ethane takes place in this case with a participation of surface oxygen of ReO_x/Alumina structure, wherein the presence of V type defects in this structure. CO_2 is formed by oxidation of methane with weekly bonded surface oxygen of the oxide. The direct oxidation of methane to methanol and further splitting of the latter to CO and H_2 is not excluded in our case.

Benzene formation on these contacts is catalyzed by ReO_x reduced with methane at high temperature. This conclusion is based on the fact that in the reaction of methane with a contact the formation of water is not found and thus the introduction of water vapor into the system leads to an increase of benzene content in the gas phase products. Disappearance of water and an increase of benzene in products of the reaction may be the result of regeneration of the structures by water molecules on the solid contact.

CONCLUSION

EPR spectroscopy in combination with chromato-massspectrometry is used for identification the active centers of oxidative conversion reaction of methane into benzene over ReO_x/Alumina catalyst. The testing of the obtained ReO_x/Alumina samples as catalysts for the oxidative conversion of methane shows that the main gas-phase products of the CH_4 conversion over these catalysts are C_6H_6, CO, C_2H_4, C_2H_6. It was found that the rhenium catalysts show the activity after high temperature oxidizing (973 K) with subsequent vacuum treatment and interaction with methane at the same temperature, but show no activity after reduction at 773 K under hydrogen current. To maintain the catalyst activity, the regeneration of the catalyst is required. Activation of the catalysts is always achieved by short term heat-treatment in oxygen atmosphere and the subsequent procedure has to be carried out in inert gas (nitrogen, argon) atmosphere to avoid the loss of rhenium in the form of volatile Re_2O_7. To regenerate the activity of the samples the treatment of catalyst by water at higher temperature is suitable also.

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